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X-RAY STUDY OF A SECOND DEHYDRATED PHASE OF COPPER AMMONIUM SULPHATE HEXAHYDRATE

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(*Received May* 26, 1965)

ABSTRACT. The existence of a second dehydration product of $Cu(NH_4SO_4)_2 6H_2O$, viz. $2[Cu(NH_4SO_4)_2]H_2O$ has been reported. The powder photograph of this phase has been indexed by De Wolffe's method. The unit cell dimensions of this monoclinic phase are $a = 16.35$Å, $b = 12.88$Å, $c = 8.77$Å, $\beta = 103°19'$ It contains 4 molecules per unit cell and the probable space groups are P2, Pm or P2/m.

INTRODUCTION

In a previous paper (Bhowmik 1961), the results of the X-ray study of $Cu(NH_4SO_4)_2\ 2H_2O$, a dehydrated phase of $Cu(NH_4SO_4)_2 6H_2O$ occurring at 65°C was reported. The thermal dehydration curve for $Cu(NH_4SO_4)_2 6H_2O$ showed another dehydrated phase which forms at 105°C and is stable upto 160°C. The dihydrate phase lost weight corresponding to a further loss of 1.1/2 molecules of water so that the new phase at 105°C contained 1/2 molecule of water of crystallisation per formula unit. The molecular formula $2[Cu(NH_4SO_4)_2]H_2O$ was assigned to it and it was further confirmed by chemical analysis.

EXPERIMENTAL

Informations regarding the crystal structure of this phase was obtained from x-ray powder photograph, since it could not be obtained as single crystals. To prepare the powder sample, a capillary tube packed with finely powdered $Cu(NH_4SO_4)_2\ 6H_2O$ was treated in the furnace at 110°C for 24 hours, so that the hemihydrate was obtained. The tube was sealed at both ends while still in the furnace, and a powder photograph was taken with a 19 cm. Unicam camera using filtered copper radiation from a Machlett tube running at 40 KV. 15m.A.

The powder photograph thus obtained was entirely different from that of the hexahydrate or the dihydrate. Also there was no spacing common with any of the following substances: $CuSO_4H_2O$, $(NH_4)_2SO_4$ or $CuSO_4$ anhydrous. Hence it was confirmed to be that of the new double salt $2[Cu(NH_4SO_4)_2]H_2O$.

Analysis of the powder pattern : Attempts were made to index the powder lines in terms of cubic, tetragonal or hexagonal systems. Since the data did not

fit with any of these systems. Lipson's method (Lipson 1949) was tried, which also did not give sufficient number of constant differences. The only remaining possibilities then were those of the salt belonging to the monoclinic or the triclinic system. In such cases of lower symmetry, both Ito's method (Ito 1950) as well as De Wolffe's method (De Wolffe 1957) may be successfully applied.

De Wolffe has shown that certain algebraic relations may be derived from Ito's equation of reciprocal lattice. With the help of these relations among the existing $Q(=1/d^2)$ values one can explore the complete reciprocal net and all its different levels.

According to the procedure of De Wolffe, we have utilised the following theoretical relations between the Q values :—1) The relation between reflections of different orders from a common lattice plane

$$n^2Q(m\,\boldsymbol{h}) = m^2Q(n\boldsymbol{h}) \qquad \ldots \quad (1)$$

where $Q(\boldsymbol{h})$ denotes the Q value corresponding to the reciprocal lattice point with radius vector $\boldsymbol{h}$; m and n are integers.

(2) Relations for a zone of lattice planes

(a) $Q(\boldsymbol{h}+\boldsymbol{h}')+Q(\boldsymbol{h}-\boldsymbol{h}') = 2[Q(\boldsymbol{h})+Q(\boldsymbol{h}')]$

(b) $Q(\boldsymbol{h}+2\boldsymbol{h}')-Q(\boldsymbol{h}-2\boldsymbol{h}') = 2[Q(\boldsymbol{h}+\boldsymbol{h}')-Q(\boldsymbol{h}-\boldsymbol{h}')]$

(c) $Q(\boldsymbol{h}+3\boldsymbol{h}')-Q(\boldsymbol{h}) = 3[Q(\boldsymbol{h}+2\boldsymbol{h}')-Q(\boldsymbol{h}+\boldsymbol{h}')]$

(d) $Q(\boldsymbol{h}+x\boldsymbol{h}')-Q(\boldsymbol{h}-x\boldsymbol{h}') = x[Q(\boldsymbol{h}+\boldsymbol{h}')-Q(\boldsymbol{h}-\boldsymbol{h}')]$

Searching for relations like (1) it was observed that $4Q_2 = Q_{18}$, $9Q_2 = Q_{32}$ and $9Q_1 = Q_{23}$, (subscripts of Q's refer to serial number of lines). Further, it was seen that if $1/4Q_1$ is taken as $Q(\boldsymbol{h}_1)$ and $1/4Q_2$ as $Q(\boldsymbol{h}_2)$ then $Q_1 = Q(2\boldsymbol{h}_1)$ $Q_6 = Q(3\boldsymbol{h}_1)$ and $Q_{23} = Q(6\boldsymbol{h}_1)$; again $Q_2 = Q(2\boldsymbol{h}_2)$, $Q_{11} = Q(3\boldsymbol{h}_2)$ $Q_{18} = Q(4\boldsymbol{h}_2)$, $Q_{25} = Q(5\boldsymbol{h}_2)$, and $Q_{32} = Q(6\boldsymbol{h}_2)$.

Thus the lines $h = 0$ and $l = 0$ in the array shown below could be written down. The figures placed at the reciprocal lattice points represent $1/d^2 \times 1000$ calculated. Those in bold types represent the Q values actually observed in the powder photograph.

Now in 2(a) we may put $\boldsymbol{h} = \boldsymbol{h}_1$ and $\boldsymbol{h}' = 2\boldsymbol{h}_2$ and since $Q_5 + Q_2 = 2Q(\boldsymbol{h}_1) + Q(2\boldsymbol{h}_2)$, we recognise Q_2 and Q_5 as $Q(\boldsymbol{h}_1 - 2\boldsymbol{h}_2)$ and $Q(\boldsymbol{h}_1 + 2\boldsymbol{h}_2)$. (The former being a case of double index).

Having obtained $Q(\boldsymbol{h}_1+2\boldsymbol{h}_2)$ and $Q(\boldsymbol{h}_1-2\boldsymbol{h}_2)$ we can and find $Q(\boldsymbol{h}_1+\boldsymbol{h}_2)$ $Q(\boldsymbol{h}_1-\boldsymbol{h}_2)$, because $Q(\boldsymbol{h}_1+\boldsymbol{h}_2)+Q(\boldsymbol{h}_1-\boldsymbol{h}_2) = 2[Q(\boldsymbol{h}_1)+Q(\boldsymbol{h}_2)] = 2(39+63\frac{1}{2}) = 205$ and $Q(\boldsymbol{h}_1+\boldsymbol{h}_2)-Q(\boldsymbol{h}_1-\boldsymbol{h}_2) = \frac{1}{2}[Q(\boldsymbol{h}_1+2\boldsymbol{h}_2)-Q(\boldsymbol{h}_1-2\boldsymbol{h}_2)] = \frac{1}{2}[339-249] = 45$ whence $Q(\boldsymbol{h}_1+\boldsymbol{h}_2) = 125$ and $Q(\boldsymbol{h}_1-\boldsymbol{h}_2) = 80$.

From these two, values of $Q(2\boldsymbol{h}_1+2\boldsymbol{h}_2)$, $Q(3\boldsymbol{h}_1+3\boldsymbol{h}_2)$ etc. and $Q(2\boldsymbol{h}_1-2\boldsymbol{h}_2)$, $Q(3\boldsymbol{h}_1-3\boldsymbol{h}_2)$ etc. were obtained using relation (1).

Now, using the various special cases of the general relation (2d), a zone of the reciprocal lattice could be built up, in which 15 of the observed Q values appeared.

k 0

l= 6				2224	2165	2185	**2284**	2462	2719	3056			
5	2356	2035	1795	1634	1552	1549	**1625**	1780	2014	2328	2719	3191	3742
4	1884	1540	1276	1103	988	961	**1014**	1146	1357	1639	2016	2462	2992
3	1579	1212	936	718	590	541	**571**	680	868	1134	1470	1906	2411
2	1400	1001	**700**	471	320	**249**	**253**	**339**	500	747	1070	1473	1955
1	1349	936	**603**	**350**	175	80	63.5	125	**268**	**489**	788	1167	1626
0	1424	975	632	356	158	39	0	39	**158**	**356**	632	975	**1424**
h=	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	1	2	3	4	5	6

Searching now for a value of $Q(h_3)$ it was observed that $\frac{1}{4}Q_9 = \frac{1}{9}Q_{18} - 131$, which however did not appear very promising. But just to test whether the lattice is monoclinic or not, zones were constructed adding 131, 4×131, 9×131 16×131 and 25×131 to the zone obtained before. In the five new zones respectively 8, 10, 9, 1 and 1 observed Q values appeared and thus all the observed values were accounted for.

k=1

l= 3	1343	1067	849	721	672	**701**	**811**	999	1265	1601	2542
3	1132	831	**602**	452	**380**	**385**	470	631	**878**	1103	2086
1	1067	734	481	**306**	211	194.5	**256**	399	620	919	1757
0	1106	763	487	289	170	131	170	289	487	763	1106
h	$\bar{5}$	4	3	$\bar{2}$	1	0	1	2	3	4	5

k= 2

l= 4	2064	1800	**1627**	1512	1485	**1538**	2304	2538	2852	**3243**	3715
3	1736	1460	1242	1114	1065	1095	1670	1881	2163	2540	**2986**
2	1525	1224	995	844	773	779	863	1024	1271	1596	1997
1	1460	1127	874	**699**	**604**	587.5	**649**	792	1013	1412	**1691**
0	1499	1156	880	682	563	**524**	563	682	**880**	1156	1499
h=	$\bar{5}$	$\bar{4}$	3	$\bar{2}$	$\bar{1}$	0	1	2	3	4	5

k=3

l= 4	2455	**2282**	2167	2140	**2193**	**2325**	2536	2818	3195
3	2115	1897	1769	1720	1750	**1859**	2047	2313	2649
2	1879	**1650**	1499	**1428**	**1432**	1518	1679	1926	2251
1	1782	1529	1354	1259	1243	1304	1447	1668	1967
0	1811	**1535**	1337	1218	**1179**	1218	1337	**1535**	1811
h=	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	1	2	3	4

k 4

l	2	2796	2567	2416	2345	2349	2435	2596	2843	3168
	1	2699	2446	2271	2176	2159.5	2221	2364	2585	2884
	0	2728	2452	2254	**2135**	2096	**2135**	2254	2452	2728
h -		$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	1	2	3	4

k 5

l =	2	3524	3528	3614
	1	**3355**	3338.5	3400
	0	3314	3275	3314
h =		$\bar{1}$	0	1

The calculated and observed Q values appear in the table.

No. of lines	Intensity	dÅ	$Q = 1/d^2$ obs.	$Q = 1/d^2$ calc.	Indices
1.	s	8.031	.0155	.0158	200
2.	w	6.318	.0251	.0253	002
				.0249	$10\bar{2}$
				.0256	111
3.	s	6.134	.0266	.0268	201
4.	w	5.729	.0305	.0306	$21\bar{1}$
5.	w	5.475	.0334	.0339	102
6.	ms	5.308	.0355	.0356	300
				.0350	$30\bar{1}$
7.	vw	5.115	.0382	.0385	012
8.	w	4.495	.0494	.0489	301
9.	vw	4.373	.0523	.0524	020
10.	s	4.285	.0545	.0541	103
11.	w	4.186	.0571	.0571	003
12.	vw	4.066	.0605	.0604	$12\bar{1}$
				.0603	$40\bar{1}$
				.0602	312
13.	ms	3.914	.0653	.0649	121
14.	s	3.785	.0698	.0702	013
				.0700	$40\bar{2}$
				.0699	$22\bar{1}$
15.	w	3.496	.0816	.0811	113
16.	vw	3.367	.0882	.0880	320
				.0878	312
17.	vs	3.231	.0956	.0961	$10\bar{4}$
18.	ms	3.133	.1019	.1014	004
				.1024	222

No. of lines	Intensity	dÅ	$Q=1/d^2$ obs.	$Q=1/d^2$ calc	Indices
19.	vs	3.049	.1076	.1072	402
20.	vw	2.914	.1178	.1179	030
21.	vvw	2.824	.1254	.1259	$13\bar{1}$
22.	vw	2.744	.1331	.1334	030
				.1335	204
23.	vvw	2.642	.1430	.1432	032
				.1428	$13\bar{2}$
				.1424	600
24.	vvw	2.551	.1537	.1538	024
				.1535	330
25.	vw	2.482	.1623	.1626	601
				.1625	005
				.1627	$32\bar{4}$
26.	w	2.425	.1695	.1691	521
27.	vvw	2.322	.1855	.1859	133
28.	vw	2.287	.1910	.1914	205
				.1906	503
29.	vvw	2.225	.2020	.2016	404
30.	vw	2.167	.2130	.2135	140
31.	ms	2.133	.2188	.2185	$10\bar{6}$
				.2193	034
32.	vvw	2.096	.2279	.2282	$33\bar{4}$
				.2284	006
33.	w	2.072	.2329	.2325	134
				.2328	305
34.	vvw	1.829	.2989	.2986	523
35.	w	1.756	.3243	.3243	424
36.	w	1.726	.3357	.3355	$15\bar{1}$

Thus we have finally established a monoclinic cell, the dimensions of the unit cell being $a = 16.35$Å, $b = 12.88$Å, $c = 8.77$Å, $\beta = 103°19'$.

No evidence of existence of glide planes and screw axes is depicted by the indices. So the possible space-group may be any of the following, $P2$, Pm, $P2/m$.

The density of the hemihydrate determined by a method described previously (Bhowmik loc. cit.) comes out as 2.20 gms per c.c. It agrees fairly well with the density 2.16 gms per c.c. calculated on the basis of 4 molecules per unit cell.

DISCUSSION

From the meagre data of a powder photograph it is not possible to throw any light on the structure of the substance. However, it may be noted that as was observed in the case of the dihydrate (orthorhombic, $b = 12.52$ Å, Bhowmik, loc. cit), the value of b remains very similar to that of the hexahydrate (monoclinic, $b = 12.50$ Å) in the case of the hemihydrate also.

ACKNOWLEDGMENT

The author expresses her sincerest thanks to Professor A. Bose, D.Sc., F.N.I., for suggesting the problem and his keen interest throughout the progress of the work. She is also thankful to Shri S. Ray, Research Officer, for general supervision and helpful discussions.

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